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April 1980

PERFORMANCE TESTS FOR THE EVALUATION OF COMPUTERIZED GAS CHROMATOGRAPHY/MASS SPECTROMETRY EQUIPMENT AND LABORATORIES

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.

- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.

- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This report was developed by the Advanced Instrumentation Section of the Environmental Monitoring and Support Laboratory. It describes a series of general purpose tests to evaluate the performance of computerized gas chromatography-mass spectrometry (GC/MS) systems. Some of the tests go beyond equipment performance and may be used to evaluate the performance of laboratories using GC/MS for organics analysis. The report will be useful to the many Federal, State, local government, and private laboratories that are planning to employ this powerful analytical tool.

Dwight G. Ballinger
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ABSTRACT

A series of ten general purpose tests are described which are used to evaluate the performance of computerized gas chromatography-mass spectrometry systems. All of the tests use the continuous, repetitive measurement of spectra method of data acquisition, and no selected ion monitoring tests are included. Evaluation criteria are given with each performance test. Some of the tests go beyond equipment performance, and may be used to evaluate the performance of laboratories using GS/MS for organics analysis.

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SECTION 1

INTRODUCTION

This report gives a series of performance tests to evaluate computerized gas chromatography - mass spectrometry (GC/MS) systems. These tests were designed for general use, and are applicable to all types of GC/MS systems. All of the tests use the continuous, repetitive measurement of spectra method of data acquisition, and no selected ion monitoring tests are included. Except for the spectrum validation test (Test I), these performance tests are not intended for routine application in a quality assurance program. Test I is a required daily quality control test for GC/MS systems in routine use for measurements of organic compounds in environmental samples. The other performance tests are intended for use in the evaluation of new GC/MS systems before purchase, or after the completion of the manufacturer's installation. These tests are also useful to evaluate GC/MS performance after a long period of downtime for extensive maintenance or repair, after a long period of equipment neglect or non-use, or as general training experiments for GC/MS operators. Several of the tests go beyond equipment performance and may be used to evaluate the performance of laboratories using GC/MS for organics analysis.

The performance tests described in this report are more rigorous and extensive than the typical manufacturer's installation tests. Indeed, this was intended, and the emphasis of the tests is on an evaluation of the total operating system in a rigorous way using experiments that closely resemble real, day-to-day operating situations. The performance tests should be conducted in the order given, but several are optional or depend on the availability of certain accessories, e.g., the solid probe inlet test.

All the tests described in this report require an operator, and some depend heavily on the skills of laboratory personnel. Therefore, the results of some tests may be limited by the skills available in the laboratory. An experienced, two-person team consisting of a professional scientist and a technician will require approximately three weeks to complete the equipment tests assuming there are no major hardware or software problems. Inexperienced teams or individuals may require anywhere from six weeks to one year to complete all the tests, especially if major hardware or software problems develop. In these tests, the operator and other laboratory personnel are a crucial part of the total operating system.

The examples given in this report reference packed column gas chromatography, but the tests described are equally applicable to open tubular GC/MS

systems. With open tubular (capillary) systems some minor adjustments in operating conditions may be necessary.

For all the tests it is assumed that the manufacturer has provided acceptable documentation of users instructions for the operation and maintenance of the GC/MS system. At the very minimum this must include clearly written descriptions of all operating and test functions, clear descriptions of all commands used in the operation of the data system, examples of all commands, and intelligible documentation of error messages. Examples of all outputs must be included as well as error recovery procedures. There must be a narrative description of all data system files, and the narrative should describe the exact nature of the algorithm used for all the significant mass spectrometric processes. The maintenance manuals must include a complete set of hardware engineering drawings, and maintenance must be described in terms of block diagrams, logic diagrams, flow charts, circuit descriptions, and parts lists.

It is also assumed that the laboratory has provided the GC/MS facility with an appropriate environment including air conditioning and other utilities as required, trained management and operating personnel, needed supplies, essential support equipment, and a reasonable amount of working space which allows access at the sides and rear of the system for maintenance.

Finally, a system logbook must be maintained throughout the evaluation period. This must include an entry for every working day noting the status of the system. This entry must be made even if the system is not used on that day, and signed by the responsible person. The logbook must include a complete record of the number of gas chromatographic injections per day, the number of solid probe samples, all chromatographic column changes, all maintenance procedures, all requirements for service from the manufacturer, and each entry must be signed and dated. This information must be summarized in the performance evaluation report, and the mean numbers of gas chromatographic injections and solid probe samples before ion source maintenance (cleaning) must be reported.

SECTION 2

SUMMARY OF PERFORMANCE TESTS

I. Spectrum Validation Test - Uses decafluorotriphenyl phosphine (DFTPP) to determine whether the system gives a 70 ev electron ionization fragmentation pattern similar to that found in the historical mass spectrometry data base, and the required mass resolution and natural abundance isotope patterns. The spectrum of DFTPP must meet the criteria given in Table 2.

II. System Stability Test - Uses DFTPP to test moderate term (20-28 hours) system stability. The criteria given in Test I must be met.

III. Instrument Detection Limit Test - Uses DFTPP to measure the full and valid spectrum detection limit at a defined and tolerable chemical noise level. At a signal/noise = 5, the required instrument detection limits are at least 50 nanograms for systems used in the analysis of industrial or municipal wastes, and at least 30 nanograms for systems used in the analysis for ambient or drinking water.

IV. Saturation Recovery Test - Uses DFTPP and p-bromobiphenyl to simulate a frequently encountered situation with real samples. The spectrum of DFTPP, measured within two minutes after the elution of a 250 fold excess of p-bromobiphenyl, must not contain significant contributions from the ions attributable to p-bromobiphenyl.

V. Precision Test - Uses a variety of typical environmental pollutants to determine precision from filling a syringe to peak integration. The mean relative standard deviation for the compounds used in the test which elute as narrow peaks must be 7% or less using either peak areas in arbitrary units or ratios of peak areas. For broad peaks the mean relative standard deviation must be 13% or less.

VI. Library Search Test - Uses data from Test V to evaluate the speed and completeness of the minicomputer library search algorithm. The mean search time, including background subtraction, must be one minute or less, and all test compounds must be identified as most probable except isomers with very similar spectra should not be counted as incorrect.

VII. Quantitative Analysis with Liquid-Liquid Extraction - Uses a variety of environmental pollutants to measure quantitative accuracy and

precision of the total analytical method. The grand average of the percentages of the true values observed must be in the 68-132% range with a mean relative standard deviation of 38% or less using either internal or external standards. This test also evaluates laboratory performance.

VIII. Quantitative Analysis with Inert Gas Purge and Trap - Uses a variety of compounds to measure quantitative accuracy and precision of the total analytical method. The grand average of the method efficiencies must be 70% or more, and all compounds must exceed 30% efficiency. The spectrum of p-bromofluoro- benzene must meet the criteria given in Table 7. The grand average of the percentages of the true values observed must be in the range of 90-110% with a mean relative standard deviation of 19% or less using either internal or external standards.

IX. Qualitative Analysis with Real Samples - Uses a real sample to evaluate the ability of the system to deal with real sample matrix effects and interferences. All compounds must be correctly identified except isomers with nearly identical mass spectra should not be counted as incorrect. This test also evaluates laboratory performance.

X. Solid Probe Inlet System Test (Optional) - Uses cholesterol to evaluate the spectrum validity achievable with a solid probe inlet system. The spectrum of cholesterol must meet the criteria given in step three of the test.

SECTION 3

EXPERIMENTAL PROCEDURES

I. Spectrum Validation Test

Correct identifications of organic pollutants from gas chromatography mass spectrometry (GC/MS) data require valid mass spectra of the compounds detected. This is prerequisite to the interpretation of the spectra, i.e., either an empirical search for a match within a collection of authentic spectra or an analysis from the principles of organic ion fragmentation. A properly operating and well tuned GC/MS is required to obtain valid mass spectra.

The purpose of this test is to make a quick check - about 15 minutes - of the performance of the total operating system of a computerized GC/MS. Thus with a minimum expenditure of time, an operator can be reasonably sure that the GC column, the enrichment device, the ion source, the ion separating device, the ion detection device, the signal amplifying circuits, the analog to digital converter, the data reduction system, and the data output system are all functioning properly.

An unsuccessful test requires, of course, the examination of the individual subsystems and correction of the faulty component. Environmental data acquired after a successful systems check are, in a real sense, validated and of far more value than unvalidated data. Environmental data acquired after an unsuccessful test may be worthless and may cause erroneous identifications.

It is recommended that the test be applied at the beginning of a work day on which the system will be used and also anytime there is a suspicion of a malfunction. A mass spectrometer which meets the criteria of this test will, in general, generate mass spectra of organic compounds which are very similar, if not identical, to spectra in collections and textbooks which have been developed over the years with other types of spectrometers. If the performance criteria of this test cannot be met by the user, the system is unacceptable for general purpose environmental measurements.

Procedure:

1. Make up a stock solution of decafluorotriphenylphosphine (DFTPP) at one milligram per milliliter (1000 ppm) concentration in acetone (or a hydrocarbon solvent). The reference compound used in this test is available from PCR, Inc., P. O. Box 1778,

Gainesville, Florida, 32602 and may be named bis(perfluorophenyl) phenylphosphine. This stock solution was shown to be 97+% stable after six months and indications are that it will remain usable for several years. Dilute an aliquot of the stock solution to 10 micrograms per milliliter (10 ppm) in acetone. The very small quantity of material present in very dilute solutions is subject to depreciation due to adsorption on the walls of the glass container, reaction with trace impurities in acetone, etc. Therefore, this solution will be usable only in the short term, perhaps one week.

2. Select a GC column for the tests. Any column that elutes DFTPP in a reasonable time may be used, and several suggested columns are listed in Table 1. Parameters should be adjusted to permit at least four mass scans during elution of the DFTPP. This will permit selection of a spectrum that is reasonably free of abundance distortions due to rapidly changing sample pressure.

3. Set the preamplifier to a suitable sensitivity and set the baseline threshold (zero instrument). Mass scale calibration is optional depending on the stability of the system -- see the last paragraph of this test.

4. Prepare for data acquisition with the following variables:

Mass Range:	40-450 amu
Scan Time:	approximately 2 to 5 seconds
Electron Energy:	70 ev
Electron Multiplier:	Not to exceed that recommended by the supplier for the age of the device.

5. Inject with a syringe 50 nanograms (five microliters) of the dilute standard into the GC column. Make appropriate concentration adjustments if an open tubular column is being used.

6. After the acetone elutes from the column and is pumped or diverted from the system, turn on the ionizer and start scanning.

7. Terminate the run after the DFTPP elutes, and plot the total ion current profile.

8. Select a spectrum number on the front side of the GC peak as near the apex as possible, select a background spectrum number immediately preceding the peak, and display the background subtracted spectrum. Some data systems permit spectrum averaging to minimize variations in ion abundance due to rapidly changing sample pressure. This option is acceptable, and may be required for narrow peaks from open tubular columns.

9. The mass spectrum can be output in various ways including a plot of the full spectrum on the plotter or cathode ray tube or a print of the full spectrum on a printer or cathode ray tube.

TABLE 1. SUGGESTED GC COLUMNS AND CONDITIONS

Dimension (Type)	Packing	Flow Rate	Temp.	R. Time
2m x 2 mm ID (Glass)	1.95% QF-1 plus 1.5% OV-17 on 80/100 mesh Gas-Chrom Q	30 ml/min	180	4 min
2m x 2 mm ID (Glass)	3% OV-1 on 80/100 mesh Chromosorb W	30 ml/min	220	5 min
2m x 2 mm ID	5% OV-17 on 80/100 mesh Chromosorb W	30 ml/min	220	5 min
2m x 2 mm ID (Glass)	1% SP2250 on 100/120 mesh Supelcoport	30 ml/min	170	5 min
30m x .25mm ID (Glass)	Wall coated SP 2100	2-5 ml/min	40,240	10 min

The spectrum obtained on the test system must meet the criteria given for the key ions in Table 2 (1).

If the relative abundances are not within the limits specified, the appropriate adjustments must be made, i.e., resolution, source potentials, calibration of the mass scale, source magnet position, etc. The manufacturer may need to be consulted for assistance in this adjustment. Repeat this test until satisfactory results are obtained. If computer controlled tuning is used but manual adjustments are required to meet these criteria, this should be noted in the evaluation report.

TABLE 2. DECAFLUOROTRIPHENYLPHOSPHINE KEY IONS AND ION ABUNDANCE CRITERIA.

Mass	Ion Abundance Criteria
51	30-60% of Mass 198
68	Less than 2% of Mass 69
70	Less than 2% of Mass 69
127	40-60% of Mass 198
197	Less than 1% of Mass 198
198	Base Peak, 100% Relative Abundance
199	5-9% of Mass 198
275	10-30% of Mass 198
365	At least 1% of Mass 198
441	Present, but less than Mass 443
442	Greater than 40% of Mass 198
443	17-23% of Mass 442

II. System Stability Test

The purpose of this test is to evaluate moderate term system stability. Repeat the test described in Section I after 20-28 hours. Do not make any adjustments or recalibration of the system between tests except routine overnight procedures. The abundance criteria in Table 2 must be met. If these criteria are not met, the system is too unstable for routine use and must be repaired.

III. Instrument Detection Limit Test

This test is to determine the smallest quantity of standard test material that can be injected into the GC/MS system that gives an acceptable spectrum meeting the criteria in Table 2, but has a sufficiently low level of background signals to allow correct interpretation of that spectrum if the sample was an unknown. Background signals are defined as mainly chemical noise that is not subtracted effectively by the background correction program. A spectrum of a test compound contaminated with background signals to the extent of about 10% or more of its total ion abundance is considered to be difficult to interpret correctly. It may be possible to find a target compund's spectrum in such a situation, but this does not constitute an interpretation of an unknown spectrum as used here. There is some variability in the 10% criteria because background distributed among a large number of small ions may be acceptable, but a distribution among a few large ions will be unacceptable. Therefore, a signal to chemical noise ratio based on a selection of six ions is used to evaluate the detection limit. This also allows a relatively simple calculation of the ratio.

In a GC/MS system there are a number of potential sources of background signals (chemical noise) including septum bleed, stationary phase bleed, vacuum system background from various physical components, and ion source contamination. Furthermore, all signals are dependent on GC column efficiency, enrichment device efficiency, vacuum system efficiency, ionization efficiency, ion transmission efficiency, and detector gain. Therefore, this test is highly sensitive to the specific system configuration (specific GC column, etc.) and the current condition of that system, e.g., condition of the GC column, extent of contamination in the ion source, extent of contamination of the quadrupole rods if a quadrupole instrument, and condition of the electron multiplier. The state of the system should be documented as part of the records of the instrument detection limit test.

Procedure:

1. Make four dilutions of the stock solution of DFTPP described in Test I. The dilutions should have the concentrations of ten micrograms per milliliter, five micrograms per milliliter, one microgram per milliliter, and one-tenth of a microgram per milliliter. Other concentrations are acceptable and may be required for open tubular columns.

2. Follow the basic procedures given in Test I and make the following

series of injections (other sequences may be used, these are examples):

Amount Injected	Volumes and Standards
50 nanograms	5 ul of 10 ug/ml standard
20 nanograms	4 ul of 5 ug/ml standard
10 nanograms	2 ul of 5 ug/ml standard
5 nanograms	1 ul of 5 ug/ml standard
1 nanogram	1 ul of 1 ug/ml standard
100 picograms	1 ul of 0.1 ug/ml standard

3. List the masses and relative abundances of the background subtracted spectra of DFTPP. Subtract the background spectra as described in Test I. If necessary use an extracted ion current profile to locate the GC peak. Discard all spectra that do not meet the criteria in Table 2. If additional dilutions or measurements are necessary, do them.

4. For each of the remaining spectra compute the ratio R as follows:

$$R = \frac{DFTPP}{BACKGD}$$

where:

DFTPP = the summation of the relative abundances of the ions at masses 127, 255, 275, 441, 442 and 443

BACKGD = the summation of the relative abundances of the six most abundant non-DFTPP background ions. Background ions with less than 3% relative abundance are assigned a value of 3. If all background is less than 3% relative abundance, this term is 18. Table 3 contains all DFTPP ions over 3% relative abundance and Table 4 contains a group of common background ions.

5. Prepare a plot of R values as a function of amount injected. The instrument detection limit defined in this test is for the complete, valid spectrum with a defined level of acceptable noise. This detection limit is the amount injected that gives an R value of five. If sufficient points are available, a good estimate of the instrument detection limit may be obtained from a first or second order regression on this data.

The rationale for the selection of an R value of five is consistent with the previous statement that background ions should be less than about 10% of the total ion abundance in an interpretable spectrum. The average relative abundance of the six DFTPP ions used to compute R is in the 25-35% range. For an R value of five the average relative abundance of the six background ions will be in the 5-7% range, and it is estimated that all background ions under these conditions will be less than 10% of the total ion abundance.

TABLE 3. IONS OVER 3% RELATIVE ABUNDANCE OBSERVED
IN THE 70 ev MASS SPECTRUM OF DFTPP

AMU	INTENSITY	PERCENT OF TOTAL INTENSITY
50.0	8.11	1.11
51.0	34.60	4.74
69.0	32.93	4.51
74.0	3.10	0.42
75.0	4.53	0.62
77.0	34.84	4.77
78.0	3.10	0.42
93.0	3.10	0.42
99.0	3.81	0.52
107.0	10.97	1.50
110.0	20.76	2.84
117.0	6.44	0.88
127.0	37.70	5.16
128.0	3.10	0.42
129.0	12.88	1.76
167.0	4.05	0.55
168.0	4.77	0.65
186.0	13.12	1.79
187.0	3.81	0.52
198.0	100.00	13.69
199.0	7.15	0.98
205.0	5.01	0.68
206.0	20.28	2.77
207.0	4.53	0.62
217.0	5.01	0.68
221.0	4.29	0.58
224.0	11.21	1.53
227.0	3.81	0.52
244.0	8.11	1.11
255.0	49.16	6.73
256.0	7.39	1.01
274.0	4.29	0.58
275.0	23.15	3.17
276.0	3.81	0.52
296.0	5.01	0.68
423.0	3.34	0.45
441.0	9.30	1.27
442.0	69.45	9.51
443.0	12.88	1.76

TABLE 4. COMMON BACKGROUND IONS IN GC/MS SYSTEMS

Masses	Sources
41,43,55,57, 69,71,81,83, 85,95,97,99	Saturated hydrocarbons and unsaturated hydrocarbons - cyclic and open chain-many sources
149	Phthalate esters used as plasticizers in tubing, etc.
73,101,135,197,207 259,345,346,355	Methyl and phenyl silicone polymers used in stationary phases, diffusion pump oil, etc.
169,261	Polyphenyl ether diffusion pump oil

The required instrument detection limits, at an R value of five, are 50 nanograms for systems used in the analyses of industrial or municipal wastes, and 30 nanograms for systems used in analyses of ambient or drinking waters. These limits were obtained from considerations of EPA recommended sample sizes and concentration factors. If a system cannot meet these criteria, maintenance or repair is required. Particular attention should be given to those items mentioned in the second paragraph of this test.

Observed detection limits with this test are as follows:

1. A Finnigan 3200 equipped with a Varian 1400 GC, a packed 1% SP 2250 Column (Table 1), a Systems Industries RIB interface, and a PDP-8 datasystem (disk) gave a detection limit of five nanograms.

2. A Finnigan 4000 with a Finnigan 9610 GC, a packed 1% SP 2250 column (Table 1), an INCOS interface, and an INCOS datasystem (Nova 3, disk) gave a detection limit of 25 nanograms.

IV. Saturation Recovery Test

The purpose of this test is to evaluate the ability of a system to measure the spectrum of a test compound at a low level immediately after a relatively large quantity of another compound entered the system. This situation occurs frequently in real environmental samples, especially waste samples where a very large concentration of one component may saturate the detector, and within a few minutes or less a very small quantity of a compound of interest may enter the detector.

Procedure:

1. Prepare an acetone solution containing five milligrams per milliliter of p-bromobiphenyl and 20 micrograms per milliliter of DFTPP. A second solution containing approximately 50 micrograms per milliliter

of each is optional and may be useful to optimize chromatographic conditions.

2. Establish GC conditions such that the DFTPP elutes within two minutes after the elution of the p-bromobiphenyl. These conditions were achieved with a 6' x 2 mm ID glass column packed with 1% SP2250 on Supelcoport (100/120 mesh) using a flow of 30 ml of helium per minute with the initial column temperature at 120°C and programming to 230°C at 10° per minute. The p-bromobiphenyl eluted at 110 seconds and the DFTPP at 210 seconds. This test is carried out using the same basic operating parameters given in Test I.

3. Inject two microliters of the standard solution containing the 250:1 ratio of p-bromobiphenyl to DFTPP. Plot the DFTPP spectrum as in Test I. Each of the ions at masses 152, 232, and 234, which are the three most abundant in the spectrum of p-bromobiphenyl, must be below 5% relative abundance in the background subtracted spectrum of DFTPP.

V. Precision Test

The purpose of this test is to measure the precision of the GC/MS system in quantitative analysis using continuous, repetitive measurement of spectra. This test evaluates precision from filling a syringe to integration of the peak area for a specific quantitation ion. The entire test should be carried out on the same day by the same technician. The application of an automatic sample changer in this test is required if it will be used for normal sample processing. This should be documented in the test results. If acceptable precision cannot be obtained with this test, the precision of a complete anaytical method may also be unacceptable.

Procedure:

1. Select a group of seven or more compounds, and prepare a standard solution in acetone that contains the entire group. Some recommended compounds are in Table 5, and the concentration of each should be 20 micrograms per milliliter. This group of compounds must include a chlorinated hydrocarbon that may decompose on a hot metal surface and a polycyclic aromatic hydrocarbon with a molecular weight greater than 200. For compounds amenable to the inert gas purge and trap procedure, prepare the standard solution in methanol at the same concentration. The purge and trap mixture must include chloroform, bromoform, sym-tetrachloroethane, and p-bromofluorobenzene. Some recommended compounds are in Tables 9-12. This test may be conducted with either or both groups of compounds.

TABLE 5. PRECISION STATISTICS FOR TEN PRIORITY POLLUTANTS PLUS OCTADECANE

COMPOUND	INTEGRATION MASS	PEAK[1] TYPE	MEAN AREA	S	(S/MEAN AREA) *100
1,3-DICHLOROBENZENE	146	N	6771	278	4.1
NAPHTHALENE	128	N	18077	375	2.1
1,2,4-TRICHLOROBENZENE	180	N	5412	195	3.6
n-OCTADECANE	254	N	345	15	4.2
DIMETHYL PHTHALATE	163	N	13540	501	3.7
DI-n-BUTYL PHTHALATE	149	N	21770	364	1.7
N-NITROSODIPHENYLAMINE	169	N	6460	228	3.5
HEXACHLOROBENZENE	284	N	4027	139	3.4
PYRENE	202	N	18107	607	3.4
CHRYSENE	228	B	10345	636	6.2
BENZO(A)PYRENE	252	B	9518	681	7.2

[1]N = narrow; B = broad (see text for definitions)

2. Select an appropriate GC column. For compounds similar to those in Table 5, the columns in Table 1 are satisfactory. For compounds, amenable to purge and trap procedures, two acceptable columns are an 8 ft. stainless steel or glass column packed with 1% SP-1000 coated on 60/80 mesh Carbopack B or packed with 0.2% Carbowax 1500 coated on 60/80 mesh Carbopack C. Prepare for data acquisition with the following variables:

   mass range: 35-350 amu (For purge and trap compounds use 20-260 amu)
   scan time: approximately two to six seconds (two or three seconds with open tubular columns)
   electron energy: 70 ev
   electron multiplier: not to exceed that recommended by the supplier for the age of the device.

3. Inject with a syringe or automatic sample changer four microliters (80 nanograms of each compound) of the standard solution and acquire data until all compounds have eluted from the column. Save the data

file on the data system and repeat the injection a minimum of four times, saving the data files in each case.

4. Plot the total ion current profiles, and use a quantitation program to integrate peak areas in arbitrary units (usually analog-to-digital counts) over a specific quantitation mass for each compound in each data file. Precision may be evaluated using either the peak areas in arbitrary units or ratios of peak areas. The former gives a precision representative of external standardization, and the latter a precision representative of internal standardization. There will be no significant difference in the results using the two methods if the system is operating properly and acceptable syringe filling and injection techniques are used. It is recommended that calculations be carried out using both methods for comparison of results, but the minimum requirement is that precision be evaluated using the method that corresponds to the standardization procedure used in the laboratory for environmental samples.

   Table 5 is an example of data from five replicate syringe injections of 80 nanograms of each compound using a Finnigan 3200 and a PDP-8 based data system. The mean areas are in analog-to-digital converter units and the standard deviations (S) were computed using the equation below. The last column in Table 5 is the relative standard deviation which is (S/mean area)* 100. Table 6 contains the results of computations with exactly the same raw data as in Table 5, but using ratios of areas as in internal standard calibrations. The response factor (RF) is defined in test VII, and the mean response factors are shown in Table 6. The compound di-n-butylphthalate was selected as the internal standard because it showed the smallest variation in peak area (1.7%, Table 5) and eluted near the mid-point in the chromatogram. The standard deviations and relative standard deviations were computed as in Table 5.

$$S = \sqrt{\frac{N \sum_{i=1}^{N} \text{Area}_i^2 - \left(\sum_{i=1}^{N} \text{Area}_i\right)^2}{N(N-1)}}$$

where:

S = the standard deviation

N = the number of measurements for each compound

Area = the integrated ion abundance of the quantitation mass

The compounds designated as having narrow peak types in Tables 5 and 6 had widths at half height of 45 seconds or less. The mean relative standard

TABLE 6. PRECISION STATISTICS USING AN INTERNAL STANDARD

COMPOUND	INTEGRATION MASS	PEAK[1] TYPE	MEAN RF	S	(S/MEAN RF) *100
1,3-DICHLOROBENZENE	146	N	0.3112	0.01512	4.9
NAPHTHALENE	128	N	0.83048	0.017250	2.1
1,2,4-TRICHLOROBENZENE	180	N	0.2486	0.008571	3.4
n-OCTADECANE	254	N	0.0158	0.000838	5.3
DIMETHYL PHTHALATE	163	N	0.62202	0.022980	3.7
DI-n-BUTYL PHTHALATE	149	N	1.00000	0.00000	0
N-NITROSODIPHENYLAMINE	169	N	0.2968	0.01008	3.4
HEXACHLOROBENZENE	284	N	0.1850	0.005899	3.2
PYRENE	202	N	0.83171	0.023110	2.8
CHRYSENE	228	B	0.4751	0.02619	5.5
BENZO(A)PYRENE	252	B	0.4370	0.0275	6.3

deviation for the data in Table 5 is 3.3%, and the corresponding mean from Table 6 is 3.6 %. Therefore there was no significant difference in the precision of external and internal standardization. The requirement of this test is that the mean relative standard deviation of data from narrow peaks be 7% or less. This requirement is based on the general observation that data from interlaboratory comparisons is usually about a factor of two more variable than single laboratory data, and this is a reasonable requirement for an acceptable system.

The last two compounds in Tables 5 and 6 gave broader peaks with peak widths at half height of more than 45 seconds. Measurements of these are more variable because of the changing baseline during temperature programming and other factors. The mean relative standard deviations from Tables 5 and 6 are 6.7% and 5.9% respectively, and internal standardization may have some slight advantage for these peaks but there are too few data points to judge the significance of this. The requirement of this test is that the mean relative standard deviation of data from broad peaks be 13% or less. Again the rule of thumb on interlaboratory data was used to establish this requirement.

If this test is conducted with compounds amenable to the inert gas purge and trap procedure, the compound p-bromofluorobenzene must be included in the mixture. This compound is a secondary spectrum validation compound which is used with GC columns that do not elute DFTPP. Therefore, after a purge and trap column is installed for this test p-bromofluorobenzene may be used as a daily check on spectrum validity. The ion abundance criteria for p-bromofluorobenzene are in Table 7, and these are consistent with the DFTPP criteria in Table 2.

TABLE 7. p-BROMOFLUOROBENZENE KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	20-40% of the base peak
75	50-70% of the base peak
95	base peak, 100% relative abundance
96	5-9% of the base peak
173	less than 1% of the base peak
174	greater than 50% of the base peak
175	5-9% of mass 174
176	greater than 50% of the base peak
177	5-9% of mass 176

VI. Library Search Test

Minimum requirements for the library search are the availability of the EPA/NIH database which is distributed through the National Bureau of Standards. The searchable database may be a subset of the EPA/NIH database, but the subset must contain at least 10,000 spectra of general and environmental interest and the Chemical Abstracts Service (CAS) registry numbers for each compound. Programs must be available to allow the operator

to submit background corrected spectra to the library search, and receive a printed report of the search results. The spectra from one of the experiments in Test V should be submitted to the library search system. Each compound must be identified as the most probable by the library search, except isomers that may have very similar 70 ev EI mass spectra should not be counted as incorrect. The mean search time, including the time for background subtraction, should be one minute or less. Printed reports should include CAS numbers. During this test make several deliberate typical operator errors, such as entry of an incorrect command and a non-existent file name. The data system should respond with an intelligible error message, and return to a logical continuation point.

VII. Quantitative Analysis with Liquid-Liquid Extraction

This test uses a variety of environmental pollutants to measure quantitative accuracy and precision of the total analytical method, but without the complications of real sample matrix effects. The test is designed for laboratories that conduct quantitative analyses of water samples with GC/MS using continuous repetitive measurement of spectra. Therefore, laboratories dealing in other media should design a similar test based on some standard reference material. The principal difference between this test and Test V, the precision test, is the consideration of potential errors and variations due to: (a) extraction of the compounds from a reagent water matrix; (b) concentration of the extract to a small volume; and (c) standardization of the measured areas in terms of the concentration of the original sample in micrograms per liter. This is one of the tests that goes beyond equipment performance, and may be used to evaluate the performance of laboratories using GC/MS for organics analysis.

It is recommended that the same standard solution of seven or more compounds that may have been prepared for the precision test (Test V) be used in this test since retention information is already available, and the concentrations are in an acceptable range. However, new standards may be used and the seven or more compounds should be at the 20 microgram per milliliter level in acetone.

Procedure:

1. Add 250 microliters (five micrograms of each compound) of the mixed standard solution in acetone to each of a minimum of five liters of reagent water. This aqueous solution is called a laboratory control standard (LCS). Set aside one additional liter of reagent water as a reagent blank.

2. Carry out the extractions according to the established procedures (2,3,4). The methylene chloride extract must be concentrated to 0.5 milliliter. The reagent blank should be measured first by itself, and if significant contamination is found, correct the problems before proceeding with this test. See the references cited above for information on the interpretation of blanks.

3. Select an appropriate column (Test V), and prepare for data acquisition using the GC/MS operating parameters given in Test V. Inject four microliters of each of the concentrated extracts, and obtain GC/MS data from each injection. Save all of the data files from the minimum of five extracts. Quantitation may be accomplished with either internal or external standardization. If an external standard will be used, this is already prepared and is the solution used to prepare the laboratory control standards. Inject two microliters (40 nanograms) of the external standard and acquire data using the same acquisition parameters.

   If an internal standard will be used, add five microliters of a one milligram per milliliter solution of the internal standard to each of the 0.5 milliliters of concentrated extract. This corresponds to the addition of five micrograms of the internal standard in such a way as to not significantly change the volume of the concentrated extract. Inject four microliters of each extract as above and save all data files. If an internal standard is used it will be necessary to measure the response factors (RF) in a separate experiment with standards (no extraction). The response factors are computed with the following equation:

$$RF = \frac{\frac{\text{Area (X)}}{\text{Amount (X)}}}{\frac{\text{Area (S)}}{\text{Amount (S)}}}$$

   where: Area(X) = the peak area of the compound in consistent units.

   Amount (X) = the quantity of the compound injected in consistent units.

   Area (S) = the peak area of the internal standard in consistent units.

   Amount (S) = the quantity of internal standard injected in consistent units.

4. Plot the total ion current profiles and use a quantitation program to integrate peak areas in arbitrary units (usually analog-to-digital converter counts) over a specific quantitation mass for each compound in each data file. If an internal standard was employed computations in terms of response factors are acceptable.

5. Precision and accuracy is expressed in terms of the percentages of the true values (P) measured in the experiments and the statistical variations in the data. The standard deviations (S) and the relative standard deviations (S/mean P) *100, are computed as described in Test 5. With an external standard P is computed as follows:

$$P = \frac{\text{area (concentrated extracts)} * 100}{\text{area (external standard)}}$$

With an internal standard P is computed with the equation below which assumes the response factors are defined as above:

$$P = \frac{\text{area (concentrated extract)} * 100}{\text{area (internal standard)} * RF}$$

Table 8 shows precision and accuracy data obtained for eight compounds extracted from reagent water with methylene chloride and measured with GC/MS using a single external standard. The GC/MS was a Finnigan model 3200 with a PDP-8 based datasystem. One difference between the data in Table 8 and the procedures described in this test is that the data in Table 8 represents duplicate extractions and measurements at four different concentration levels between 15-200 micrograms per liter for each compound. Figures 1 and 2 show control charts which contain all eight P values for each of two of the compounds. This is a recommended method (5) of displaying precision and accuracy data. Charts should be labelled as in Figures 1 and 2. General experience shows that P values measured over a concentration range of one or two orders of magnitude are often concentration independent within the precision of the method.

The mean of the P values (grand average) in Table 8 is 84%. Therefore, the requirement of this test is that the grand average P value of the compounds used in this test must be in the range of 68-132%. Again, as in Test V, the expectation is that multi-laboratory data will usually be about a factor of two more variable than single laboratory data. The mean relative standard deviation from Table 8 is 19%, and the requirement of this test is that the mean relative standard deviation be 38% or less.

VIII. Quantitative Analysis with Inert Gas Purge and Trap

This test uses a variety of environmental pollutants to measure quantitative accuracy and precision of the total analytical method, but without the complications of real sample matrix effects. The test is designed for laboratories that conduct quantitative analyses of water samples with GC/MS using continuous repetitive measurement of spectra. Therefore, laboratories dealing in other media should design a similar test based on some standard reference material. The principal difference between this test and Test V, the precision test, is the consideration of potential errors and variations due to: (a) purging of the compounds from a reagent water matrix; (b) trapping and desorption of the compounds; and (c) standardization of the measured areas in terms of the concentration of the original sample in micrograms per liter. This test is required to evaluate purge and trap equipment that is delivered as an integral part of a GC/MS system, or other purge and trap equipment that is interfaced to the GC/MS system.

The series of experiments in this test is used to generate three key pieces of information about purge and trap performance:

TABLE 8. PRECISION AND ACCURACY DATA FOR LIQUID-LIQUID EXTRACTION WITH GC/MS AND AN EXTERNAL STANDARD

COMPOUND	INTEGRATION MASS	MEAN P	S	(S/MEAN P) *100
NITROBENZENE	123	94	8.8	9.4
1,2,3-TRICHLOROBENZENE	180	85	13	15
NAPHTHALENE	128	73	18	25
ACENAPHTHYLENE	152	83	15	18
N-NITROSODIPHENYLAMINE	169	89	19	21
FLUORANTHENE	202	80	19	24
PYRENE	202	83	19	23
n-BUTYLBENZYLPHTHALATE	206	86	17	20

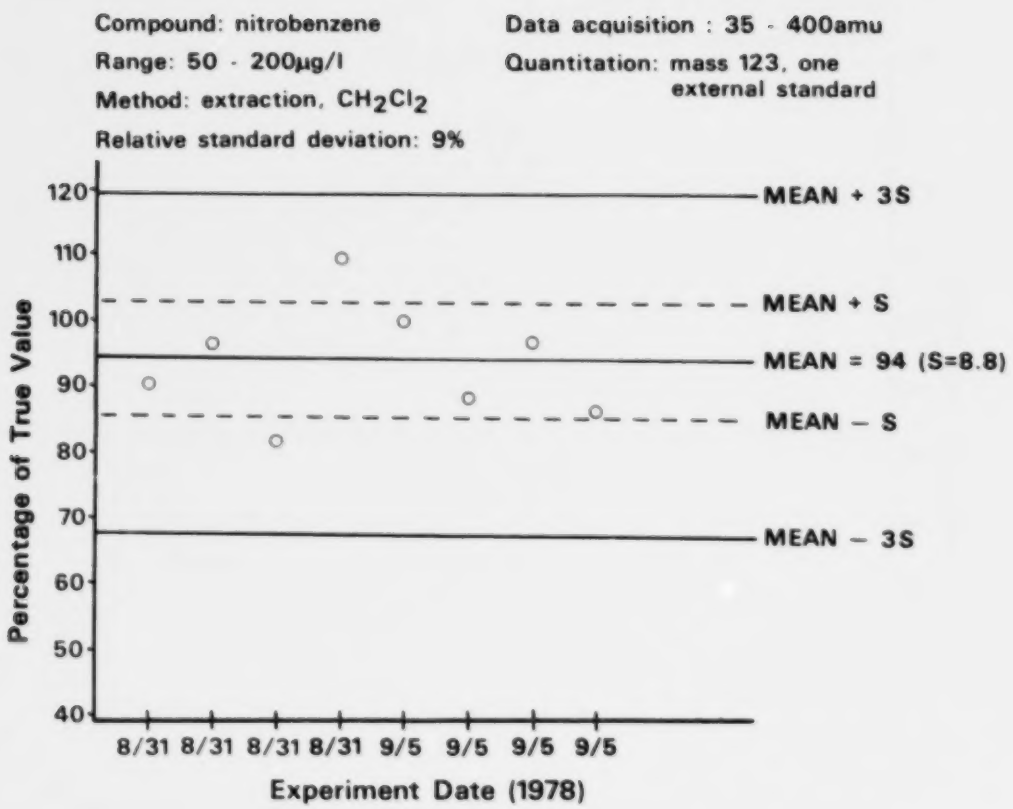

Figure 1. Control chart for nitrobenzene in reagent water.

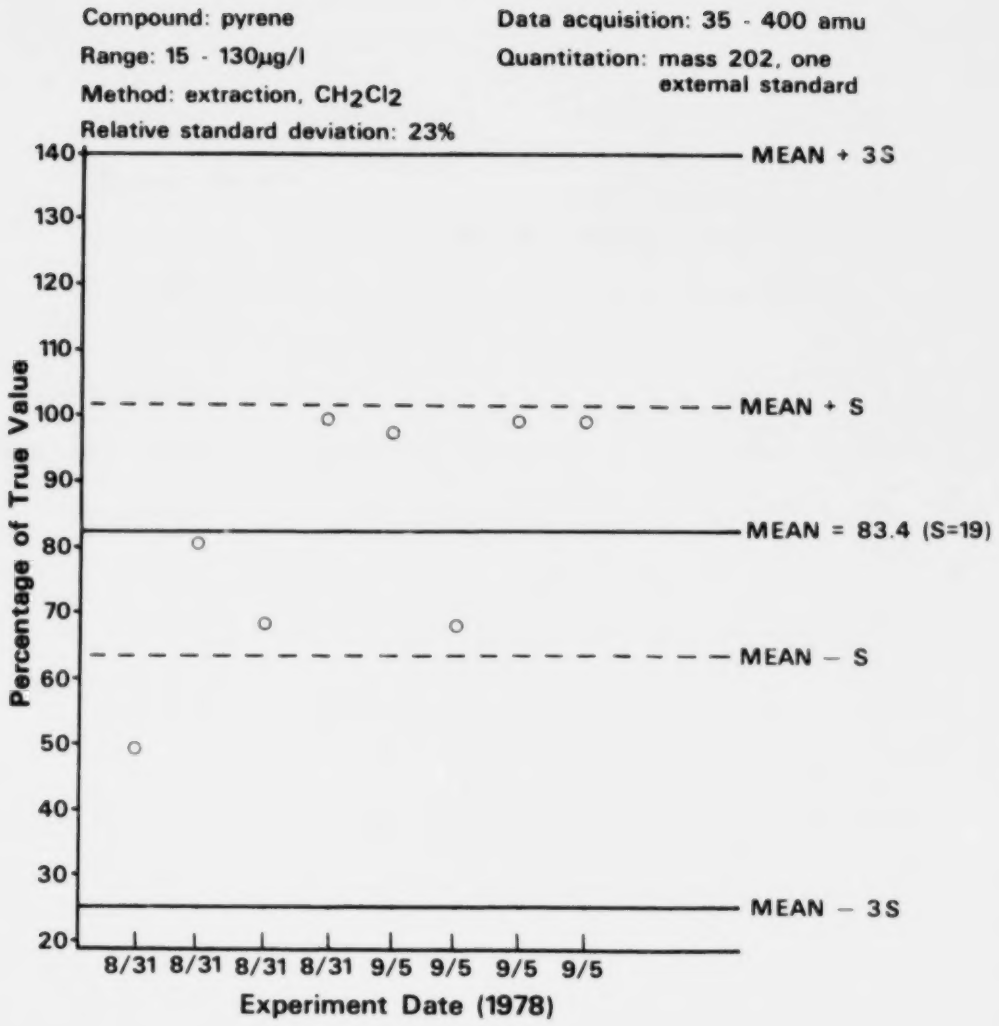

Figure 2. Control chart for pyrene in reagent water.

(a) Method efficiency for test compounds by comparison of the measured quantity from syringe injection into the GC with the quantity measured after purging, trapping, and desorption. Because of the method of calibration used in the purge and trap procedure high method efficiency as defined above is not necessary for acceptable precision and accuracy. However, high method efficiency is required for acceptable sensitivity, and low method efficiency will result in unacceptable detection limits. Also in the case of real samples, a low method efficiency combined with an unfavorable matrix effect could render the method totally useless.

(b) Precision of the overall purge, trap, desorption, and GC/MS analysis.

(c) Accuracy of the overall purge, trap, desorption, and GC/MS analysis in terms of the percentage of the true value found in laboratory control standards.

All the above information may be obtained from the same set of data. It is recommended that the same standard solution of seven or more compounds amenable to purge and trap that was recommended for the precision test (Test V) be used in this test since retention information may be already available, and concentrations are in an acceptable range. However, new standards may be used, and the seven or more compounds should be at the 20 micrograms per milliliter level in methanol. The purge and trap mixture must include chloroform, bromoform, sym-tetrachloroethane and p-bromofluorobenzene.

Procedure:

1. Select an appropriate column (see Test V) and prepare for data acquisition using the GC/MS operating parameters given in Test V.

2. Add five microliters (100 nanograms of each compound) of the mixed standard in methanol to each of a minimum of five aliquots of reagent water. A zero dead volume syringe is strongly recommended for this transfer. Purge and trap samples may be 5 ml to 25 ml, but 5 ml is recommended for optimum method efficiency. This aqueous solution is called a laboratory control standard.

3. Carry out the purge and trap according to the established procedures (2,3,4) at ambient temperature. A reagent water blank should be measured first and at occasional intervals to detect instrument contamination. If significant contamination is found, correct the problems before proceeding with this test. See references cited above for information on the interpretation of blanks.

4. Purge, trap, desorb, and obtain GC/MS data from a minimum of five laboratory control standards and save all the data files. At about the midpoint of the purge and trap analyses, inject with a syringe five microliters (100 nanograms of each compound) of the mixed standard in methanol into the purge and trap GC column. A zero dead

volume syringe is strongly recommended for this injection. Acquire GC/MS data using the same acquisition parameters used for purge and trap analyses.

5. Plot the total ion current profiles, and use a quantitation program to integrate peak areas in arbitrary units (usually analog-to-digital converter counts) over a specific quantitation mass for each compound in each data file.

6. Method efficiency must be evaluated by comparing the measured areas from direct GC injection with the corresponding areas from the purge, trap, and desorption experiments. Internal standards cannot be used for this evaluation because method efficiencies for various compounds are not yet known, and comparable response factors cannot be computed for direct injection and purge/trap/desorption.

   Prepare a table similar to Table 9 which shows data obtained with a Finnigan model 3200, a PDP-8 data system, and a Tekmar model LSC-1 purge and trap device with a 25 ml sample container. The equation used to compute method efficiencies (E) is shown below. The minimum requirement of this test is that the mean of the mean (grand average) method efficiencies of the compounds used in this test be 70% or more and all compounds must be recovered with at least 30% efficiency. Also the spectrum obtained from p-bromofluorobenzene must meet the ion abundance criteria given in Table 7. If these requirements cannot be met, the system is unacceptable for quantitative analyses and needs repair or redesign. One critical method variable that may be optimized is the purge gas flow rate.

$$E = \frac{\text{area (after purge and trap)}}{\text{area (direct injection)}} * 100$$

7. Precision and accuracy data may be obtained by choosing one of the experiments in the purge and trap set as a standard, and computing the percentages of the true values (P) measured in the other laboratory control standards. This is consistent with the standard method of calibration used with the purge and trap method. The experiment chosen as the standard may either be treated as an external standard, or may be used to compute response factors for an internal standard calibration. Table 10 shows the data from the method efficiency determination recomputed by ignoring the direct injection result, and using one of the purge and trap experiments as an external standard. The equation used to compute the percentages of the true values (P) is as follows:

$$P = \frac{\text{area (after purge and trap)}}{\text{area (external standard)}} * 100$$

   The standard deviation of P and relative standard deviation were computed as described in Test V. The mean of the P values (grand average) in Table 10 is 95% and the mean relative standard deviation

TABLE 9. METHOD EFFICIENCIES FOR SOME PRIORITY POLLUTANTS PLUS p-BROMOFLUOROBENZENE

COMPOUND	INTEGRATION MASS	MEAN AREA PURGE/TRAP	AREA DIRECT INJECTION	MEAN METHOD EFFICIENCY(%)
CHLOROFORM	83	2883	3001	96
CARBON TETRACHLORIDE	117	2289	2314	99
BROMODICHLOROMETHANE	83	2925	3280	89
TRICHLOROETHYLENE	130	1474	1653	89
DIBROMOCHLOROMETHANE	129	1572	2343	67
BROMOFORM	173	1241	2788	45
TETRACHLOROETHYLENE	166	1737	2102	83
Sym-TETRACHLOROETHANE	83	1032	3071	34
p-BROMOFLUOROBENZENE	174	1542	2200	70

TABLE 10. PRECISION AND ACCURACY DATA FOR THE PURGE AND TRAP ANALYSIS WITH GC/MS AND AN EXTERNAL STANDARD

COMPOUND	INTEGRATION MASS	MEAN P	S	(S/MEAN P) *100
CHLOROFORM	83	92	8.8	9.5
CARBON TETRACHLORIDE	117	97	7.9	8.2
BROMODICHLOROMETHANE	83	96	7.2	7.5
TRICHLOROETHYLENE	130	94	7.4	7.9
DIBROMOCHLOROMETHANE	129	98	4.4	4.5
BROMOFORM	173	96	5.2	5.4
TETRACHLOROETHYLENE	166	96	14	14
Sym-TETRACHLOROETHANE	83	100	14	14
p-BROMOFLUOROBENZENE	174	90	12	14

is 9.4%. The requirement of this test is that the grand average of the P values of the compounds used in this test must be in the range of 90-110%. This is based on the general rule, described in Test V, that data from interlaboratory comparisons is usually about a factor of two more variable than single laboratory data. The mean relative standard deviation must be 19% or less on the same basis.

The percentages of the true values (P) may also be computed by selecting one compound in the test mixture as an internal standard, and using one of the purge and trap experiments to establish response factors as defined in Test VII. The percentages of the true values (P) in the other laboratory control standards are computed as follows (the terms have the same meaning defined in Test VII):

$$P = \frac{\text{area } (x) * 100}{\text{area } (s) * RF}$$

Table 11 shows the method efficiency data recomputed with p-bromofluorobenzene as the internal standard. Response factors were established with the same purge andd trap experiment that was used as an external standard for the computations in Table 10. Table 12 shows the same data recomputed with dibromochloromethane as an internal standard. Again, response factors were established with the same purge and trap experiment that was used as an external standard for the computations in Table 10.

The internal standard calculations reveal that the percentages of the true values observed and the relative standard deviations are a function of the internal standard selected. The compound p-bromofluorobenzene eluted late in the chromatogram after temperature programming, and measurements of it were more variable because of this and other factors. This is reflected in the grand average of the P values from Table 11 of 108% and the mean relative standard deviation of 12%. The compound dibromochloromethane showed the least variation in the external standard data (Table 10) and is an excellent internal standard. The grand average of the P values from Table 12 is 97% with a mean relative standard deviation of 6.5%. This illustrates that care must be exercised in the selection of an internal standard because of the potentially significant impact on the observed precision and accuracy. The individual P values may also be charted as in Figures 1 and 2 to provide a graphic presentation of the data.

IX. Qualitative Analysis with Real Samples

The purpose of this test is to evaluate the ability of the GC/MS system, laboratory, and sample preparation methods to deal with natural background, interferences, and sample matrices found in real environmental samples. The test is limited to qualitative analyses because of the unpredictable quantitatvie effects of the sample matrix. This is one of the tests that goes beyond equipment performance, and it may be used to evaluate the performance of laboratories using GC/MS for organics analysis. The test is designed for laboratories that conduct qualitative analyses of water samples with GC/MS using continuous, repetitive measurement of spectra.

TABLE 11. PRECISION AND ACCURACY DATA FOR THE PURGE AND TRAP ANALYSIS WITH GC/MS AND THE INTERNAL STANDARD p-BROMOFLUOROBENZENE

COMPOUND	INTEGRATION MASS	MEAN P	S	(S/MEAN P) *100
CHLOROFORM	83	103	13	13
CARBON TETRACHLORIDE	117	108	12	11
BROMODICHLOROMETHANE	83	107	12	11
TRICHLOROETHYLENE	130	105	12	11
DIBROMOCHLOROMETHANE	129	110	11	10
BROMOFORM	173	108	12	11
TETRACHLOROETHYLENE	166	107	13	12
Sym-TETRACHLOROETHANE	83	112	19	17
p-BROMOFLUOROBENZENE	174	100	0	0

TABLE 12. PRECISION AND ACCURACY DATA FOR THE PURGE AND TRAP ANALYSIS WITH GC/MS AND THE INTERNAL STANDARD DIBROMOCHLOROMETHANE

COMPOUND	INTEGRATION MASS	MEAN P	S	(S/MEAN P) *100
CHLOROFORM	83	94	5.8	6.2
CARBON TETRACHLORIDE	117	98	4.3	4.4
BROMODICHLOROMETHANE	83	98	3.7	3.7
TRICHLOROETHYLENE	130	95	3.8	4.0
DIBROMOCHLOROMETHANE	129	100	0	0
BROMOFORM	173	98	2.0	2.0
TETRACHLOROETHYLENE	166	98	9.8	10
Sym-TETRACHLOROETHANE	83	101	11	11
p-BROMOFLUOROBENZENE	174	92	9.7	11

Procedure:

1. Acquire appropriate quality control samples containing a number of organic compounds dissolved in acetone, methanol, or other water-miscible organic solvent and sealed in all-glass ampuls. The concentration levels should be suitable for the preparation of aqueous samples in the 10-500 microgram per liter range by addition of one ml or less of the organic solution to the environmental sample. Instructions for the dilutions should be supplied with the samples, but the identity of the compounds in the ampuls should be supplied separately to the laboratory management. A number of samples of this type will be available in 1980 from:

   Quality Assurance Branch
   EMSL-Cincinnati
   Environmental Protection Agency
   Cincinnati, Ohio 45268

2. Obtain an environmental sample typical of the type normally analyzed in the laboratory. Add the quality control samples to the environmental samples according to the instructions provided, and proceed with the analyses using the appropriate method, e.g., as in Tests VII and VIII.

3. Plot the total ion current profiles and identify all the compounds using the mass spectra. All compounds must be correctly identified except, as in the library search, isomers with nearly identical 70 ev electron ionization spectra should not be counted as incorrect.

X. Solid Probe Inlet System Test (optional)

The purpose of this test is to evaluate the critical thermal characteristics of the solid probe inlet system, and to determine whether valid spectra are produced with this system. The test uses cholesterol which is sensitive to thermal effects. Data acquisition is by continuous repetitive measurement of spectra.

Procedure:

1. Prepare a standard solution of cholesterol in acetone at a concentration of 250 micrograms per milliliter. Evaporate one microliter of this solution in the solid probe sample holder.

2. Use the data acquisition parameters given in Test I, and gradually heat the sample until the cholesterol pressure increases and spectra may be measured.

3. Terminate data acquisition and plot a background subtracted spectrum of cholesterol as described in Test I. Measure the abundances of the ions at masses 386 and 368, and compute the 386/368 abundance ratio. This should be 3.0 or greater for an acceptable solid probe inlet system. The ion abundance at mass 387 should be 26-34% of the

abundance at mass 386. Finally large ions above 30% relative abundance should be at masses 41, 43, 55, 57, 67, 69, 71, 79, 81, 83, 91, 93, 95, 105, 107, 109, 119, 121, 133, 145, 147, 149, 159, 161, 213, 275, 301, and 386.

SECTION 4

REFERENCES

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